



Measurement of V_{50} Behavior of a Nylon 6-Based Polymer-Layered Silicate Nanocomposite

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Abstract

The performance under ballistic impact conditions of a nylon 6-based polymer-layered silicate (PLS) nanocomposite was examined using a V_{50} test. The commercially available nanocomposites contained approximately 2.5-wt.% montmorillonite clay mineral and were fabricated by *in situ* polymerization of ϵ -caprolactam in the presence of an organosilicate clay mineral. The velocity at which 50% of 0.22-cal. fragment simulator projectiles penetrated the unmodified nylon 6 and 0.5-mm aluminum witness plate (V_{50}) was determined to be 436 ft/s. The PLS nanocomposite nylon 6-clay hybrid was found to have a V_{50} of 338 ft/s. Therefore, it was found that the addition of the layered silicate clay mineral filler did not improve the impact properties of nylon 6 under these conditions.

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1. Introduction

In 1987, researchers at Toyota Central Research and Development in Japan began patenting and later publishing in the open literature research detailing work done with a novel, polymer-based composite system comprised of nylon 6 and layered silicate clay minerals including montmorillonite [1-9]. This material was found to have significantly improved mechanical properties, barrier properties, and thermal properties, which make it a candidate material for Army applications requiring a high performance, lightweight material.

The Toyota material is the prototypical polymer-layered silicate (PLS) nanocomposite system. PLS nanocomposites are composite materials having a polymer matrix with a layered silicate clay mineral filler which usually totals no more than 5 wt.% of the final product [10]. The Toyota material is filled with 2.5-wt.% montmorillonite, a 2:1 layered silicate clay mineral similar to mica and talc [11]. Montmorillonite is comprised of individual silicate layers 1 nm in thickness and on the order of 1 μm in the lateral dimension. These silicate layers stack together to form clay particles called tactoids, with the gaps between individual layers called galleries [11, 12]. The individual silicate layers are crystalline and are comprised of three sublayers—a layer of aluminum hydroxide octahedra edge shared with two layers of silicon hydroxide tetrahedra (see Figure 1). Isomorphous substitution of magnesium for aluminum and aluminum for silicon in the crystal structure leads to a net charge within the layers, which is balanced by the presence of hydrated cations in the galleries. Sodium, calcium, potassium, and lithium are common interlayer cations.

Cation exchange reactions are often used to replace these naturally occurring cations with alkylammonium cations, which facilitate the penetration of polymer into the silicate galleries. It has been shown empirically that modification of the clay mineral with an organic surfactant facilitates the formation of an exfoliated morphology, which is critical to achieving substantial improvements in physical properties.

Kojima et al. [8] reported dramatic improvements in the mechanical, thermal, and barrier properties of nylon 6 after modification of the polymer with 4.7 wt.% montmorillonite. These included a 91% increase in the tensile modulus, a 55% increase in tensile strength, and an increase of 80 °C in the heat distortion temperature. Impact strengths have been reported to be improved, but over all have been found to be decreased [8, 10]. The Toyota researchers also collected data indicating that the nylon 6-hybrid material had decreased permeability. Their work showed a 37% decrease in the water adsorption characteristics of

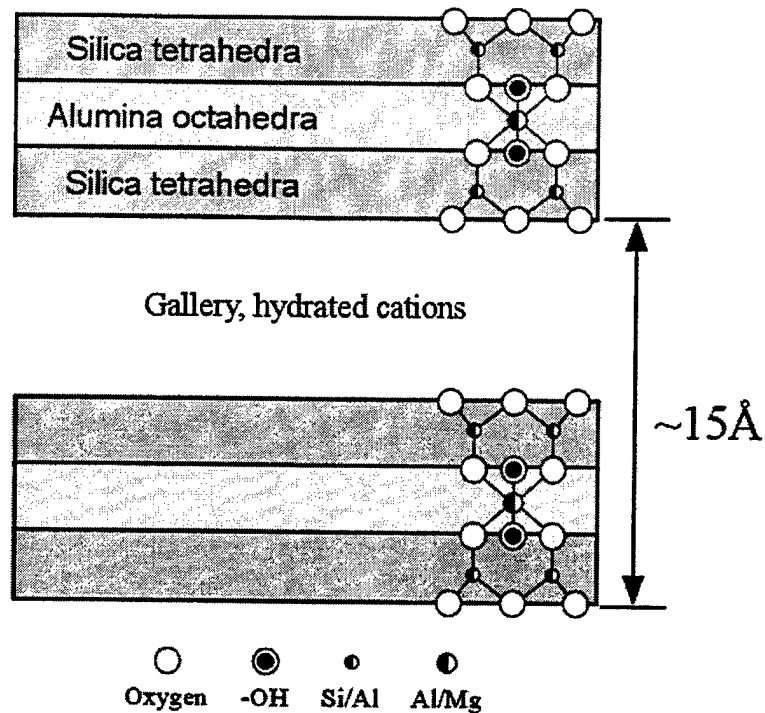


Figure 1. Illustration of two crystalline silicate layers of montmorillonite with interlayer gallery of approximately 5 Å.

nylon 6 as well as improvements in other systems [9, 13]. Additionally, more recent work on this class of materials indicates that the formation of a nanocomposite significantly improves the ablative properties of the material [14, 15].

As a result, it is anticipated that a PLS nanocomposite system based on montmorillonite and nylon 6 would be a good candidate material for certain U.S. Army applications. The improved mechanical properties suggested that the ballistic properties of the modified clay might be noteworthy. Other characteristics, such as the decreased permeability and improved ablative properties, may allow the nanocomposite material to be used for multiple purposes including chemical and biological threat protection applications. Enhanced thermal stability has already been proven to allow use of these materials in automotive applications including gasoline tanks, oil tanks, air ducts, and intake manifolds, cylinder head covers, timing belt covers, power steering, and fluid reservoirs [2, 4].

For the purpose of establishing an initial estimate of the behavior of PLS nanocomposites in lightweight armor applications, a set of tests to determine the V_{50} of the unmodified nylon 6 and PLS nanocomposite based on nylon 6 were undertaken. These tests approximately followed the MIL-STD-622F [16] standard for determining this property.

2. Experimental

Unmodified nylon 6 and the nylon 6-based PLS nanocomposite materials were obtained from the UBE-Hanna Compounding Company, LLC, New York, NY. The materials are designated by UBE as 1015B for the unmodified nylon 6 and 1015C2 for the PLS nanocomposite and are nearly identical in composition and fabrication to those used by Kojima et al. [8, 17] and Usuki et al. [18]. The hybrid material is produced by the *in situ* polymerization of ϵ -caprolactam containing approximately 2.5-wt.% montmorillonite which has been modified with alkylammonium cation surfactants based on amino carboxylic acid.

Fabrication of plaques suitable for ballistics tests were fabricated using an HPM 90-ton injection molder. Both materials were dried 4 hr at 74 °C. Barrel temperatures ranged between 440 °F and 500 °F, with the nozzle temperature being the highest. Injection velocity was 2 in/s at 1000 psi, while the mold temperature was held between 150 °F and 180 °F. Plaques produced in this manner were approximately 3.44 in wide, 6.79 in long, and 1/8 in thick. After several weeks' storage in an atmosphere of approximately 50% relative humidity, the areal density of the unfilled nylon was determined to be 2.9 mg/mm², while the nanocomposite was found to have an areal density of 3.0 mg/mm².

Ballistic tests were performed following Department of Defense standard MIL-STD-622F [16]. In these tests, 0.22-cal., 1.1-g fragment simulator projectiles (FSP) were propelled at the target using a helium-pressurized gas gun described elsewhere [19, 20]. Projectile velocities were determined by recording the time differential between the penetration of two pieces of silver grid paper using an electronic chronograph. Impacts were made at zero degrees obliquity, and the extent of penetration of the projectile was determined by visual inspection of a witness plate located 6 in behind the target. A calculation of the V_{50} velocity was made after an equal number of complete and partial penetrations of the target were recorded in the same velocity range.

To determine average water content, thermogravimetric analysis (TGA) was performed using a TA Instruments 2950 Thermogravimetric Analyzer. Samples were brought to 110 °C and held isothermally for 240 min. Water content was determined directly from equilibrium weight loss. Clay content was also determined by TGA, where a sample of the hybrid material was heated to complete decomposition of the organic phase.

3. Results

Visual inspection of plaques manufactured from both the unmodified nylon 6 and nylon 6-based PLS nanocomposite clearly revealed that the two materials were not equally processible. While both materials were predried under the same conditions, the unmodified nylon 6 formed plaques of low quality; voids were visually evident and numerous in the unmodified material. The majority of plaques manufactured from the nylon 6-based PLS nanocomposite were of better quality with fewer voids. This was contrary to expectations based on the effect on gas permeation in PLS nanocomposites, but may be attributed to the thixotropic nature of smectite clays.

TGA results from both materials indicate slight water adsorption. The unmodified nylon 6 was found to have 1.9% water by weight. The PLS nanocomposite material was found to contain 2.1% water by weight. The total weight-percent of clay mineral in the hybrid material was indeterminate. TGA results indicated that approximately 3.8 wt.% of the hybrid material was inorganic, whereas 1.9 wt.% of the unmodified nylon 6 was inorganic. This suggests that approximately 2% of the hybrid material was layered silicate.

The results of the ballistics testing are listed in Table 1. The unmodified material was found to have a higher V_{50} , 436 ft/s, than the nanocomposite material, which was found to have a V_{50} of 338 ft/s. Both samples displayed significant spalling and radial fracture.

Table 1. Ballistics properties of nylon 6 and a nylon 6-based PLS nanocomposite.

Sample	V_{50} (ft/s)	8 Shot Spread (ft/s)
1015B (nylon 6)	436	10
1015C2 (hybrid)	338	12

4. Discussion

The lower V_{50} of the modified nylon 6 is consistent with the physical characteristics of the plaques observed during sample preparation. The modified system appeared to be more brittle than the unmodified nylon 6. This result is not inconsistent with the impact behavior of the clay hybrid reported in the literature; while some references described the modified material as having

better impact resistance, most show decreased toughness consistent with the behavior observed here. The observed spalling is also an undesirable behavior because fragments of an armor material can be as dangerous as a projectile; a ductile response to penetration would be preferable.

5. Conclusions

V_{50} tests were performed on commercially available nylon 6 and nylon 6-based PLS nanocomposite materials. The data showed a decrease by 22% in the velocity required for 50% penetration of a 0.22-cal. fragment projectile on a witness plate, according to testing standard MIL-STD-622F [16]. These results are consistent with the observed toughnesses of the two materials and toughness data reported in the literature.

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W DRYSDALE
G GAZONAS
S GHIORSE
D GRANVILLE
D HOPKINS
C HOPPEL
D HENRY
R KASTE
M KLUSEWITZ (10 CPS)
M LEADORE
R LIEB
E RIGAS
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W SPURGEON
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6. AUTHOR(S) David Ostermayer,* Frederick L. Beyer, Peter G. Dehmer, and Melissa A. Klusewitz				
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13. ABSTRACT(Maximum 200 words) The performance under ballistic impact conditions of a nylon 6-based polymer-layered silicate (PLS) nanocomposite was examined using a V_{50} test. The commercially available nanocomposites contained approximately 2.5-wt.% montmorillonite clay mineral and were fabricated by <i>in situ</i> polymerization of ϵ -caprolactam in the presence of an organosilicate clay mineral. The velocity at which 50% of 0.22-cal. fragment simulator projectiles penetrated the unmodified nylon 6 and 0.5-mm aluminum witness plate (V_{50}) was determined to be 436 ft/s. The PLS nanocomposite nylon 6-clay hybrid was found to have a V_{50} of 338 ft/s. Therefore, it was found that the addition of the layered silicate clay mineral filler did not improve the impact properties of nylon 6 under these conditions.				
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